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CHEMISTRY DEPARTMENT
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Summary of work done in the period
November 1, 1966 to April 30, 1967

THEORETICAL STUDY OF THE ATOMIC AND MOLECULAR GASES AND THEIR REACTIONS IN THE UPPER ATMOSPHERE

Submitted to the National Aeronautics and Space Administration, Washington, 25, D. C. The report contains a brief summary of the work done during the period November 1, 1966 to April 30, 1967

Roop C. Sahni

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Project Director

PERSONNEL

Dr. R. C. Sahni	Chief Investigator and Project Director
Dr. C. D. La Budde	Research Scientist
Dr. D. C. Jain	Assistant Research Scientist
Dr. B. C. Sawhney	Assistant Research Scientist
Dr. M. J. Hanley	Assistant Research Scientist
Mrs. Ida Kelly	Secretary

INTRODUCTION

In the previous report it was stated that we have extended our 'auto vary' programs to include 3s and 3p functions in addition to 1s, 2s and 2p functions for the computation of the potential energy curves of the different states of the diatomic molecules. In that report we have also stated that our predicted work on the unknown NF molecule, which was reported in the NASA Progress Report N65-857-71, April 1965 and later in NASA CR-688, has been confirmed experimentally and reported by A. E. Douglas and W. E. Jones at the Symposium on Molecular Structure and Spectroscopy at Columbus, Ohio, U.S.A. on September 1966. Recently A. E. Douglas and W. E. Jones have published a paper in the Can. J. Physics., 1966, 44, 2251 and have confirmed our theoretically predicted results for the R_e (equilibrium distance) and excitation energy of b $^1\Sigma^+$ state in addition to the ground state of NF which they confirmed previously. Our theoretical work on NF has also been accepted in the Transactions of the Faraday Society. Our work on the unknown NF molecule has thus confirmed the soundness of our work on the quantum mechanical computation of the wave functions and potential energy curves of the different states of diatomic molecules.

We are now developing programs for the configuration interaction treatment and also for determining the properties of the diatomic molecules. We hope to report some of these results in the coming report. We owe much of the success of this work to the excellent computing facilities and cooperation of the personnel of the Institute for Space Studies, 2880 Broadway, New York, New York and the Goddard Space Flight Center, Greenbelt, Maryland.

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Work carried out during the above period can be given under the following headings:

(1) Computation of the Excited States of CO Molecule.

(2) Calculation of the Wave Functions and Potential Energy Curves of the Hydrides of the First Group of the Periodic Table with Complete Set 1s, 2s and 2p for Both Atoms.

(3) Calculation of the Wave Functions and Potential Energy Curves of the Ground and Ionized States of N_2 Molecule.

(4) Development of Molecular Constant Programs.

(5) Development of the 'Properties-Integrals' Programs for the I.B.M. 360-70 Computer.

(1) Computation of the Excited States of CO Molecule.
by R. C. Sahni and B. C. Sawhney

In previous reports we have stated that we have carried out the quantum mechanical treatment of the ground and ionized states of CO and computed their potential energy (P.E.) curves. We have extended this treatment to the excited states of CO. As in the previous calculations we have optimized both the LCAO coefficients and the screening constants of the atomic orbitals (A.O.) in these calculations. A number of calculations have been carriedoout to find if it were possible to compute the various excited states from the same set of screening constants to avoid optimizing the screening constants of every state at each internuclear distance. For this purpose each of the states has been computed by optimizing its screening constants individually as well as with the optimized screening constants of the ground state of CO. The details of these calculations will be discussed in the coming report.

(2) Calculation of the Wave Functions and Potential Energy Curves of the Hydrides of the First Group of the Periodic Table with Complete Set 1s, 2s and 2p for both Atoms.
by R. C. Sahni, C. D. La Budde and B. C. Sawhney

In the previous report it was mentioned that since the hydrides are the simplest diatomic molecules, with hydrogen atom on one nucleus, it is intended to carry out extensive calculations of these molecules to understand the structure of diatomic molecules. In general, the calculations carried out on hydrides have involved only 1s orbital on hydrogen and very seldom attempts have been made to include 2s and 2p AO's on hydrogen atom. We have for our computation included complete set of 1s, 2s and 2p orbitals for both atoms. Our calculations are in a way using a large extended set of orbitals than hitherto used for these

hydrides. We are still working on some of these hydrides and hope to describe the details of the results in the coming report.

(3) Calculation of the Wave Functions and Potential Energy Curves of the Ground and Ionized States of N_2 Molecule.
by R. C. Sahni, C. D. La Budde and B. C. Sawhney

In one of the previous reports we mentioned that we have succeeded in extending our calculations to include 3s and 3p functions. We also described the complexity of the problem that we have to calculate 4398 integrals instead of 523 integrals required without inclusion of 3s and 3p functions. Moreover, the integrals involving 3s and 3p functions are much more complex and tedious to calculate. Since these extended calculations involve several times more computer time than the calculation with the limited set, we have extensively developed programs to cut down the computer time. We are happy to report that we have succeeded in this attempt and the computation with the extended set is now manageable with the present computer facilities. We have carried out successfully some calculation on the ground and ionized states of N_2 molecule. We hope to report some of this work in the coming report.

(4) Development of Molecular Constant Programs.
by D. C. Jain and R. C. Sahni

In the previous report it was stated that Dr. D. C. Jain was busy in transforming his molecular constant programs from the I.B.M. 7094 computer to the I.B.M. 360-70 computer. All these programs are now working in double precision. Dr. D. C. Jain has used his programs to a number of problems. He has successfully carried out the variation of transition moment in some band systems of the N_2 molecule. This work has been accepted for publication in the Journal of the Quantitative Spectroscopy and Radiation, Pergamon Press Ltd. and will shortly appear. A brief summary of this work is given below:

"The variation of the electronic transition moment with the internuclear separation has been studied in the first positive, the second positive and the Vegard-Kaplan band systems of N_2 by using the Franck-Condon factors based on the Rydberg-Klein-Rees potential energy curves. The 'smoothed' relative band strengths and the relative intensities at infinite temperature have also been reported for these band systems."

(5) Development of the 'Properties-Integrals' Programs for the I.B.M. 360-70 Computer.
by B. C. Sawhney and M. J. Hanley

In the previous report it was stated that 'Properties Integrals' programs were near completion for I.B.M. 360-70 computer. These programs deal with both Homo-polar and Hetero-polar molecules. So far these programs were limited to 1s, 2s and 2p functions. During the period of this report these

programs have been extended to include 3s and 3p functions. Once our potential energy curves for different states of N_2 with extended set containing 3s and 3p functions are computed we will use these programs to compute the properties of diatomic molecules.

PUBLICATIONS

(a) During this period the following papers of the group have been published:

1. Quantum Mechanical Treatment of Molecules. Part 2.—Calculation of the Potential Energy Curves and Molecular Constants of the X $^2\Sigma^+$, A $^2\Pi$ and B $^2\Sigma^+$ Ionized States of CO, by R. C. Sahni and B. C. Sawhney, Trans. Faraday Soc., 63, 1, (1967).

2. Transition Probability Parameters of the Band Systems of CO^+, by D. C. Jain and R. C. Sahni, J. Quant. Spectrosc. Radiat. Transfer, 6, pp 705-715, Pergamon Press Ltd.,(1966).

3. Quantum Mechanical Study of Molecules: Prediction of the Ground, Ionized and Excited States of the Unknown NF Molecule, by R. C. Sahni, NASA CR-688, January 1967.

(b) The following papers have been accepted for publication:

1. Quantum Mechanical Treatment of Molecules. Part 3.—Prediction of Electronic States of NF by A Comparative Study of the Electronic States of N_2, CO, O_2 and NF Molecules, by R. C. Sahni, Trans. Faraday Soc.

2. Einstein A Coefficients, Oscillator Strengths and Absolute Band Strengths for the First Negative System, and Franck-Condon Factors for the Second Negative System of N_2^+, by D. C. Jain and R. C. Sahni, Int. J. of Quant. Chem.